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Study of Waste Lubricant Hydrocracking into Fuel Fraction over The Combination of Y-Zeolite and ZnO Catalyst

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Abstract

The study of waste lubricant hydrocracking into gasoline and diesel fraction using the combination of Y-Zeolite and ZnO (Y-Zeolite/ZnO) catalyst has been conducted. The hydrocracking of waste lubricant was carried out in a semi-flow stainless steel reactor system (i.d = 3.78 cm; l = 30 cm) with hydrogen stream (20 mL/min) at 573, 623, and 673 K. The characterization of catalysts including crystallinity was analysed by X-Ray diffraction (XRD), the amount of total acid site was determined by gas sorption method, the surface area was measured by BET method, and the morphology of the catalyst was analyzed by Transmission Electron Micrograph (TEM). The activities of catalyst including total convertion, liquid and gas product (yield), and selectivity for gasoline and diesel fractions were evaluated. Total convertion was defined as (100–residue)%. The liquid product was collected and analyzed by gas chromatography (GC) and flame test. The characterization using XRD showed that ZnO could be rested upon the Y-Zeolite by wetblending. The amount of total acid sites of the Y-Zeolite/ZnO was higher than the constituent material. The highest total convertion of the lubricant using the Y-Zeolite/ZnO was 99.49 wt.% while the Y-Zeolite was 99.10 wt.% at 623 K and without catalyst (thermal hydrocracking) was 98.99 wt.% at 673 K. The highest liquid product at 623 K was achieved by the Y-Zeolite/ZnO catalyst (24.75 wt.%) with the selectivity for gasoline and diesel fractions was 25.92 and74.08 %.

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Keywords: waste lubricant; hydrocracking; Y-Zeolite; ZnO; fuel fraction

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1. Introduction

Waste treatment has become one of the most important concerns in the field of environment conservation by the modern society. As the global reserves of fossil fuel are finite, great efforts are made to find alternative carbon sources to be used as fuels. Most of the works reporting the pyrolysis of waste primarily focused on the solid waste from different sources, for example, such as used tyres [1] and plastic waste [2].

Lubricant consumption is getting increased each year due to its importance in various applications. Large volumes of waste lubricant oil are considered hazardous wastes. This is because the oil waste typically consists of a mixture of un-degradable base oil and additives which have high concentrations of metals, varnish, gums, and other asphaltic compounds [3]. Waste lubricant is often either burnt or disposed in an uncontrolled landfill. These alternatives are unacceptable for the environmental damage it might be caused, since the waste lubricant oils contain numerous additives that are harmful to human health [4]. The presence of polyaromatic heteroatom substances, sulphur, chlorine, and bromine [5] in waste lubricant oil also poses serious problems if one wants to use it as a fuel or any other applications. As a solution, waste lubricant could be collected and processed via a re-refining process to become "re-refined lubricating oil" with an equivalent quality to new lubricating oil [6, 7, 8] or via direct upgrade from thermal cracking or catalytic cracking.

In thermal cracking, hydrocarbons with higher molecular weight in lubricating oils can be transformed to lighter hydrocarbon products by thermolysis at higher temperature, which is then accompanied by the formation of coke; large amount of gas and naphtha with lower quality would also be produced due to overcracking [3]. Adding catalysts into the cracking process will decrease the decomposition temperature while promoting the decomposition kinetics; hence, it would make the whole process more efficient while it would also reduce pollution by decreasing energy consumption and minimizing unnecessary products and by-products, such as heteroatom substances.

Catalytic cracking of waste lubricant over solid acids (zeolites, silica-alumina, MCM-41, clays, etc.) to yield different hydrocarbon fractions has been proposed by several authors as a promising alternative for fuel production [4,5,9]. Zeolites have been regarded as one of the most important catalysts in the petrochemical industry due to their excellent chemical properties [10,11] to act as a catalyst, such as acidity, thermal stability and have pores whose size is large enough to allow reactants readily access their surface. From all types of zeolites, the Y-type is still the most important zeolite to be used as catalyst for its high concentration of active acid sites, high thermal stability and high size selectivity [12,13].

Many researchers have attempted zeolite modification in order to obtain the optimum number and strength of acid sites in zeolite and also a suitable pore structure having high activity and selectivity. The impregnation of ZnO into Natural Zeolite Active (ZAAH) has been studied as a catalyst that could increase liquid product yield from hydrocracking lubricant [5]. Blending ZnO into Y-Zeolite also has excellent sulphur removal activity and selectivity [14]. In the present study, we report the recycling of waste lubricant oil via hydrocracking over ZnO catalysts supported by Y-Zeolite. The objective of the present investigation was to study the effect of variables such as temperature, the effect of the catalyst combination, and catalyst pore size to the liquid product selectivity in terms of gasoline and diesel fractions.

2. Experimental

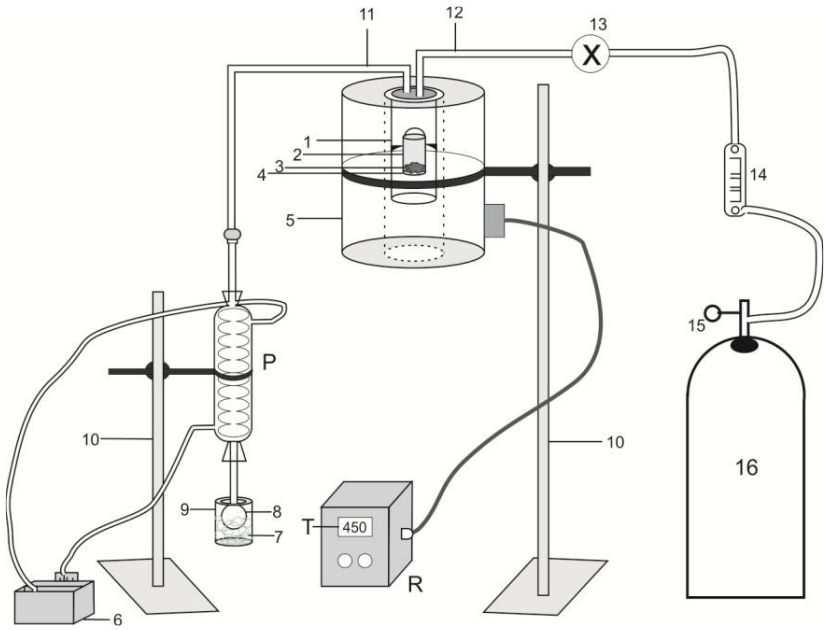
The waste lubricant oil used in the present study was collected from local auto shop (Yogyakarta, Indonesia). The obtained waste lubricant oil was highly viscous, then was filtered using qualitative filter paper (Whatman No. 42 equivalent) and was centrifuged with the rotation speed of 2000 rpm for 30 min to remove the solids phase. The treated waste lubricant oil then was used as a sample for thermal and catalytic treatment in present study. The thermal treatment of waste lubricant oil was carried out in the absence of catalyst. Y-Zeolite/ZnO catalyst was prepared by wet (mass ratio of Y-Zeolite:ZnO= 1) blending, using 10% methanol for 24 h. The prepared catalyst sample was dried at 383 K for 3 h and calcined using 450 watt microwave Sharp 900 W for 60 min.

A semi flow-fixed bed system (i.d=3.78 cm; l=30 cm) (Fig.1) operated at atmospheric pressure and made of stainless steel was used for testing the thermal and catalytic hydrocracking of waste lubricant oil. The hydrocracking process was carried out with ratio of catalyst to feed ratio to be 1:5 with hydrogen flow of 20 mL/min for 1 h. The reaction temperature was varied from 573, 623, and 673 K (Table 1). The surface area of the catalysts was determined by BET method (Quantachrome), using nitrogen physisorption at –196 °C and taking 0.162 nm^2 as cross sectional area of N_2 molecule. X-ray diffraction (Shimadzu XRD-6000) studies were carried out on using graphite

filtered Cu Kα radiation. The distribution of ZnO over the Y-Zeolite catalyst was characterized by Transmission Electron Micrograph (TEMJEM-1400). Commercial gasoline and diesel fuel were used as standards for the qualitative estimation of gasoline and diesel fractions. The composition of liquid products then was analysed by Gas Chromatography (Agilent Technologies 6890N). The gaseous products were trapped in sealed syringe, then were analysed qualitatively by using flame test and calculated (wt.%) by comparing the mass percentage of liquid, coke, and residue by mean of (100 – liquid – coke – residue).

Table 1. Various treatments on waste lubricant oil hydrocracking process.

Treatment	Catalyst	Temperature (K)
A	Thermal	673
B	ZnO	573
C		623
D		673
E	Y-Zeolite	573
F		623
G		673
H	Y-Zeolite/ZnO	573
I		623
J		673



P = Refrigerator
R = Electrical regulator
T = Digital thermometer
1 = Reactor and feed container
2 = Catalyst container
3 = Catalyst
4 = Kassa
5 = Furnace tube
6 =Electrical motor
7 = Ice beaker
8= Product container
9 = Ice container
10 = Statif
11 = Gas product out
12 = H_2 in
13 = One way kran
14 = H_2 flowmeter
15 = Regulator
16 = H_2 container

Fig. 1. Schematic experimental setup for the thermal and catalytic hydrocracking of waste lubricant oil.

3. Results and Discussion

3.1. Y-Zeolite/ZnO Preparation

The catalyst treatment was carried out by wet blending at atmospheric pressure. The characterization of various catalysts employed in the present study was carried out for BET surface, and for morphology of the catalysts was carried out by powder XRD. The results are given in Table 2 and Fig.2. It is clear from Table 2 that Y-Zeolite (575.94 m^2/g) has higher surface area than ZnO (4.95 m^2/g) and Y-Zeolite/ZnO (237.86 m^2/g). The difractograms in Fig.2 shows that the catalyst treatment was found ZnO phase in Y-Zeolite. The distribution of the ZnO over the Y-Zeolite particle was also studied by TEM. The TEM results given in Fig.3 show the presence of large ZnO crystallites on the outside of the Y-zeolite particles. They were located on the surface of the Y-Zeolite particles which covered most of the Y-Zeolite surface with them. The fibers like in Fig.3 represents Y-Zeolite particles which have high crystallinity and the ZnO was shown in black region.The acidity (ZnO, Y-Zeolite, and Y-Zeolite/ZnO) for the surface and total acidity were also taken and the results are presented in Table 3. It is confirmed that the acidity increased after the combination process. However, there was only a little difference between Y-Zeolite/ZnO (3.48 mmol/g) and Y-Zeolite (3.42 mmol/g) acidity.

Table 2. Characteristics of catalysts pores.

Catalyst	Total radii volume (cc/g)	Surface area (m^2/g)	Mean pore radii (Å)
ZnO	0.01	4.95	48.78
Y-Zeolite	0.36	575.94	12.57
Y-Zeolite/ZnO	0.18	237.86	15.15

Table 3. The surface and total acidity of prepared catalysts.

Catalyst	Acidity (mmol/g)	
	Surface	Total
ZnO	0.06	1.81
Y-Zeolite	1.02	3.42
Y-Zeolite/ZnO	1.11	3.48

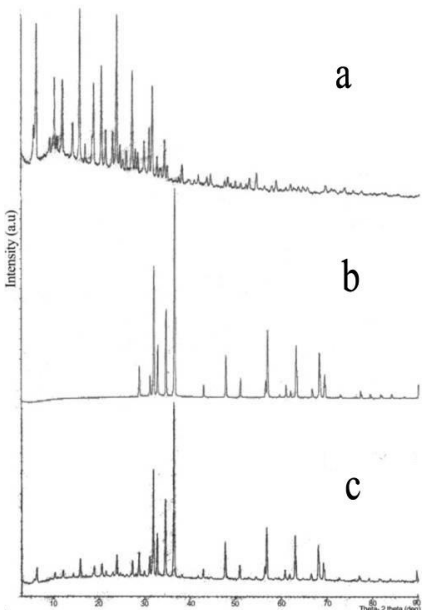


Fig.2. XRD difractrograms of : (a) Y-Zeolite, (b) ZnO, and (c) Y-Zeolite/ZnO catalysts.

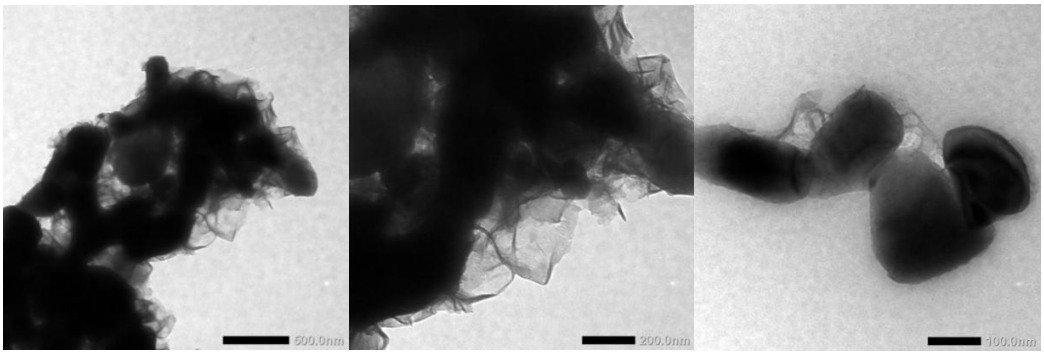


Fig.3. TEM Images of Y-Zeolite/ZnO catalyst

The thermal hydrocracking of waste lubricant oil was carried out only in one temperature (673 K) at atmospheric pressure. The catalytic hydrocracking of waste lubricant oil was carried out by using ZnO, Y-Zeolite, and Y-Zeolite/ZnO catalysts at various temperatures (573, 623, and 673 K) at atmospheric pressure. Generally, all of the hydrocracking produced three main products: liquid, gaseous, and coke. The results are presented in Table 4. Liquid products were collected and analyzed by Gas Chromatography. Flame test was carried out in gaseous products to identify their flammability. Gaseous products were considered to be light fraction of alkane with dominant composition of propane and butane.

Thermal hydrocracking produced the highest liquid fraction (31.25 wt.%) than other catalytic hydrocracking. This was due to the formation of radical free which happened in thermal hydrocracking, whereas the catalytic hydrocracking went with different mechanism. In this study, waste lubricant consisted of poliaromatic molecules. Using high temperature in thermal treatment was not enough to crack the aromatic ring. On the other hand, in catalytic hydrocracking, the aromatic ring could be protonated by catalyst. Consequently, the feed was easier to be cracked by catalyst and also thermal condition. That phenomenon caused catalytic hydrocracking produced more lighter fraction in gaseous phase than that of thermal hydrocracking.

Low temperature (573 K) hydrocracking on all catalysts used produced the lowest amount of liquid fractions. High amount of residue in this condition indicates that polyaromatic molecules were not cracked well. The reaction condition did not provide sufficient energy for the movement of the molecules to react, yielding the fewest liquid fractions (see Table 4).

Table 4 shows that the hydrocracking on 623 K gave the optimum value for liquid fraction on ZnO and Y-Zeolite/ZnO catalysts. This might due to the pore size of each catalyst which was higher than Y-Zeolite. Higher energy and pore size allowed the feed molecules to enter the catalyst pore easier and rupture C-C bond. However, Y-Zeolite catalyst showed its liquid fraction optimum value on higher temperature (673 K). This may due to the smallest pore radius on Y-Zeolite which was harder for molecules to enter and needed higher energy to be in the catalyst pores.

Table 4.Distribution of waste lubricant oil hydrocracking product.

Treatment	Product Distribution (wt.%)				Total Conversion
	Liquid	Coke	Gaseous	Residue	
Thermal	31.25	0.00	67.74	1.01	98.99
ZnO/573	2.79	2.39	92.83	1.99	98.01
ZnO/623	10.81	2.50	85.96	0.73	99.27
ZnO/673	5.78	2.90	90.41	0.91	99.09
Y-Zeolite/573	3.82	33.06	60.13	2.99	97.01
Y-Zeolite/623	7.77	31.79	59.54	0.90	99.10
Y-Zeolite/673	8.20	32.10	58.64	1.06	98.94
Y-Zeolite/ZnO/573	4.90	11.49	81.63	1.99	98.01
Y-Zeolite/ZnO/623	24.75	13.17	61.57	0.51	99.49
Y-Zeolite/ZnO/673	3.99	11.63	83.61	0.77	99.23

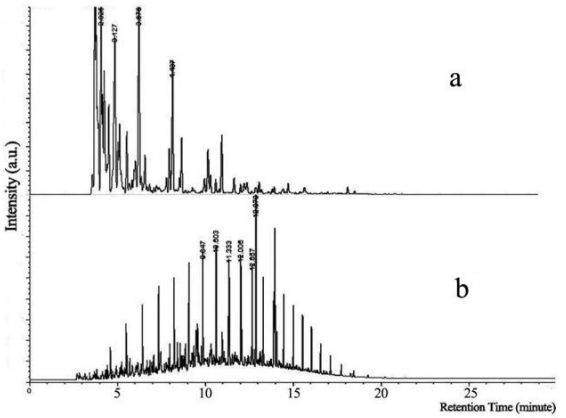


Fig.4.Gas-chromatograms of : (a) commercial gasoline and (b) diesel.

The three catalysts showed higher gaseous fraction on every temperature condition especially on 623 K. Hence, it is shown that all reaction condition accelerated the conversion of waste lubricant oil into gaseous fraction. However, thermal hydrocracking gave more liquid fraction than catalysed hydrocracking. The catalysts activity for liquid fraction conversion was not as good as in thermal condition.

3.2. Catalyst selectivity in terms of gasoline and diesel fractions

The liquid products obtained from hydrocracking of waste lubricant were analyzed by GC to determine the composition of the hydrocarbons. The results of thermal and catalytic hydrocracking were compared with commercial gasoline and diesel gas-chromatograms (see Fig.4). The total ion chromatogram (up to retention time of 25 min) of waste lubricant, before and after the thermal treatment, is presented in Fig.5. It is clear from Fig.5 that the increase of low molecular weight hydrocarbons was prominent. It appeared from the sharp peaks in gas-chromatograms at retention time less than 15 minutes. However, the character of waste lubricant oil was still observed. On the other hand, the catalytic hydrocracking drastically increased the low molecular weight hydrocarbons by the presence of sharper peaks. The results are given in Fig.7 and Fig.8.

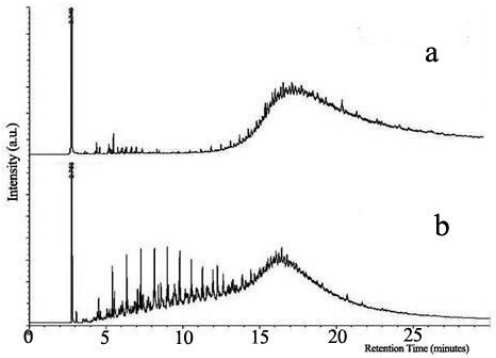


Fig.5.Gas-chromatograms of : (a) waste lubricant oil and (b) liquid product over thermal hydrocracking.

Liquid product selectivity over thermal and catalytic hydrocracking is shown in Fig.9. Selectivity in terms of gasoline and diesel fractions was determined through comparation between each peak area and total area fractions. Gasoline (C_5-C_{12}) fractions were observed from the sharp peaks in gas-chromatograms at retention time less than 10 minutes representing n-dodecane. Retention time above 10 minutes represents diesel fractions, which have carbon number more than 12. It is clear from Fig.9 that hydrocracking over Y-Zeolite catalyst produced the highest gasoline fractions. It indicates that Y-Zeolite catalyst was more selective in term of gasoline fractions. That was due to the acid sites on Y-Zeolite surface. The protic acid site (Bronsted acid) initiated the carbenium ion [15] formation on that polyaromatic chain. Through the Protonated Cyclopropane Mechanism (see Fig.6), there would be a hydride shift in the carbenium ion resulting a transition condition of cyclopropane which would form a very reactive carbenium intermediate of tertiary carbenium ion. The intermediate carbenium was then protonated by hydrogen and cracked into branched hydrocarbon short chain (gasoline fraction) and straight hydrocarbon long chain (diesel fraction). Higher acid sites on Y-Zeolite allowed more Protonated Cyclopropane Mechanism and gave more gasoline fraction. ZnO with less acid site which resulted in less formation of the tertiary carbenium ion [16], yielding more straight chain of diesel fractions.

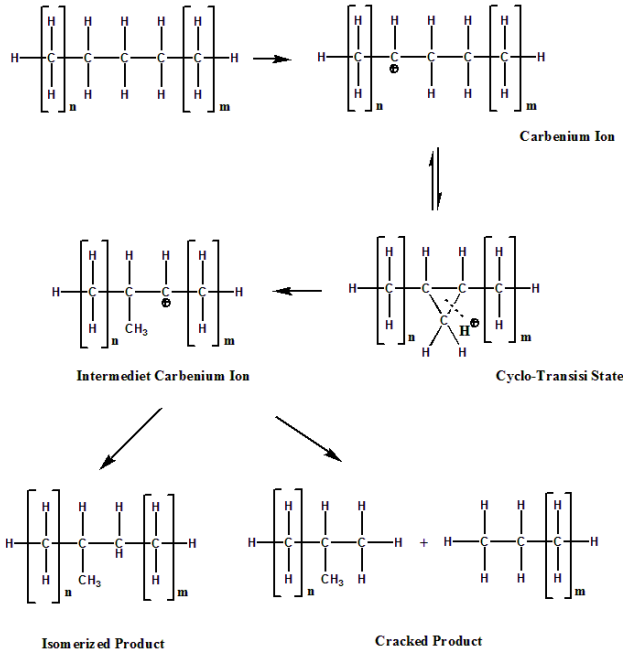


Fig.6. The reaction mechanism of hydrocracking process

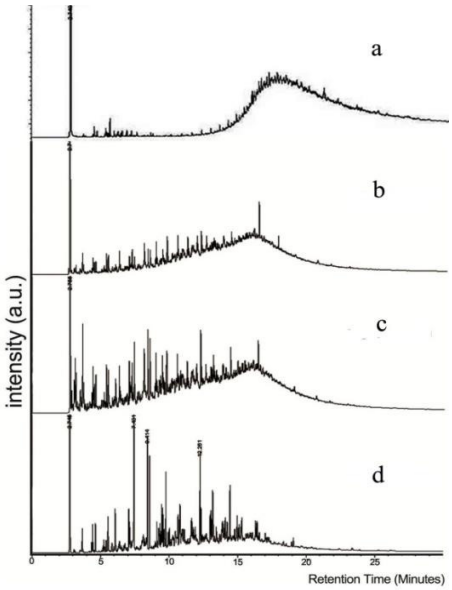


Fig.7. Gas-chromatograms of : (a) waste lubricant oil , (b) Y-Zeolit 573 (c) Y-Zeolite 623 and (d) Y-Zeolite 673.

Note : The symbol of catalyst Y-Zeolite 573 indicated the hydrocracking of catalyst followed by temperature (K).

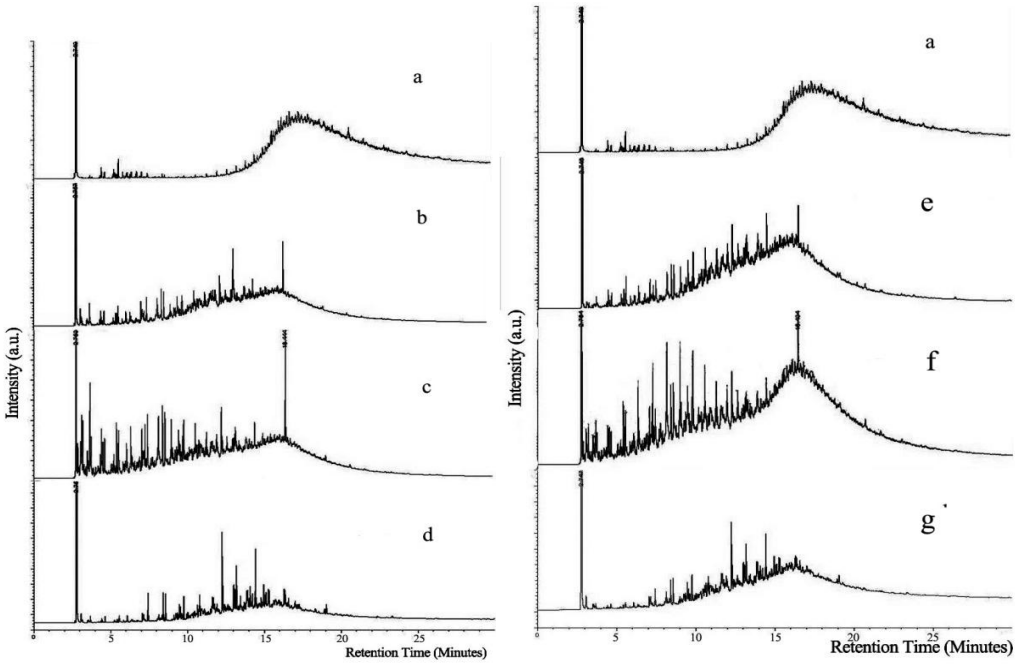


Fig.8. Gas-chromatograms of : (a) waste lubricant oil , (b) ZnO 573, (c) ZnO 623, (d) ZnO 673, (e) Y-Zeolite/ZnO 573, (f) Y-Zeolite/ZnO 623 and (g) Y-Zeolite/ZnO673.

Note : The symbol of catalyst ZnO573 and Y-Zeolite/ZnO 573 indicated the hydrocracking of catalyst followed by temperature (K).

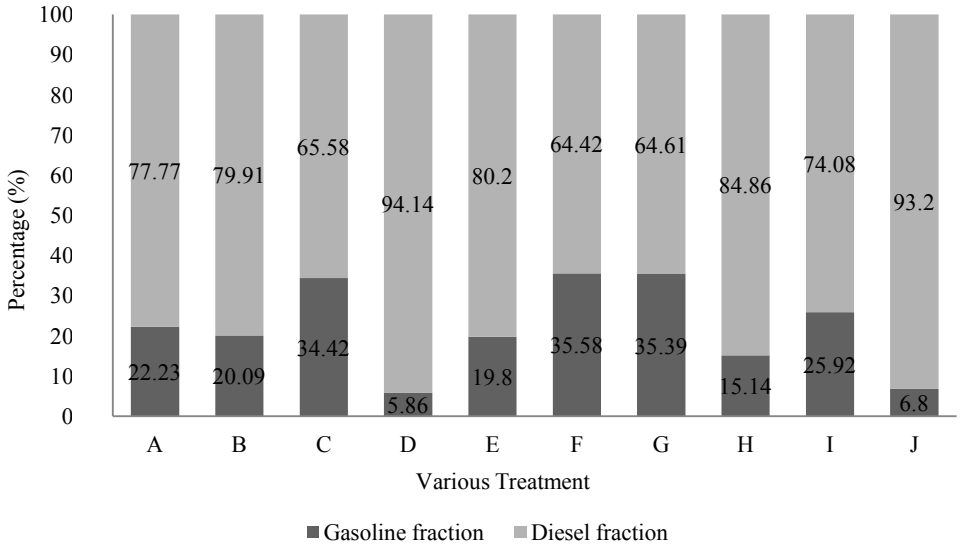


Fig.9. Liquid product selectivity for gasoline and diesel fraction.

Note : Definition of A-J see table 1.

In the case of ZnO catalyst, high temperature could lead to sintering process so that metal would coagulate. As a result, surface area of the catalyst decreased and the active sites on the surface catalyst would be closed [5]. It caused the hydrocracking reaction using ZnO catalyst led to achieve heavier fractions (diesel fractions). The liquid product of hydrocracking over Y-Zeolite/ZnO catalyst was more selective on diesel fractions too. This might due to the ZnO character. TEM images (in Fig.3) confirmed that ZnO covered the Y-Zeolite surface. It made the acid sites on Y-Zeolite more unaccessible. Therefore, the carbenium formation by the acid sites was not optimum and the mechanism happened was likely similar to the mechanism on ZnO catalyst.

The hydrocracking reaction over ZnO catalyst had high selectivity for diesel fractions (65.58 %). However, the maximum of the total conversion of liquid product was 10.81 wt.% at 623 K (see Table 4). On the other side, the selectivity of Y-Zeolite/ZnO catalyst for diesel fraction (74.08 %) was higher than using the ZnO catalyst with the total conversion of liquid product was 24.75 wt.% at 623 K (see Table 4). It indicates that blending of ZnO into Y-Zeolite pore could increase the total liquid product for hydrocracking reaction. This result shows that the Y-Zeolit/ZnO catalyst was more effective and economic to be used and it had high selectivity for diesel fractions at 623 K.

4. Conclusion

Blending of ZnO into Y-Zeolite (mass ratio of Y-Zeolite:ZnO = 1) decreased the character of Y-Zeolite. The ZnO was located on the surface of the Y-Zeolite particles which covered most of the Y-Zeolite surface. The acidity of catalytic hydrocracking increased after the combination process. The highest total convertion of the lubricant using the Y-Zeolite/ZnO catalyst was 99.49 wt.% while the Y-Zeolite was 99.10 wt.% at 623 K and without catalyst (thermal hydrocracking) was 98.99 wt.% at 673 K. The highest liquid product at 623 Kwas achieved by Y-Zeolite/ZnO(24.75 wt.%) with the selectivity for gasoline and diesel fractions was 25.92 wt.% and 74.08 wt.%.The Y-Zeolite catalyst was more selective for gasoline fractions, whereas the ZnO and Y-Zeolite/ZnO catalysts was more selective for diesel fractions.

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